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RECENT EXPERIMENTAL DEVELOPMENTS IN RETORTING OIL SHALE AT THE LAWRENCE LIVERMORE LABORATORY

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"Recent Experimental Developments in Retorting Oil Shale at the Lawrence Livermore Laboratory"

Abstract

The Lawrence Livermore Laboratory is engaged in a program aimed at extraction of oil from oil shale _in-situ_. The experimental program is briefly described. Retorting results obtained in pilot above-ground retorts are reviewed. Combustion retorting of small (1-2 cm) particles of narrow size distribution gives yields near 95% of assay, and appears to be reasonably understood and predictable by model calculations. Results on retorting behavior of non-uniform sized particles are less well understood. Reasons for this behavior are examined, and appear to be related to non-uniform gas flow. The effect of steam on retorting is considered.

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The Lawrence Livermore Laboratory is engaged in research and development of a modified in-situ process to obtain oil from oil shale. The term "modified" refers to the removal of a fraction of the oil shale by mining to permit the formation of blocks small enough and voids sufficient for adequate heat transfer and fluid flow during the recovery operation. The plan calls for development of underground columns of oil shale rubble by modified sublevel caving.[1] The top of the rubble bed is ignited, and air is pumped down to sustain burning. The hot gases so produced flow down through the rubble, pyrolyzing the organic material (kerogen) to oil and gaseous species, leaving behind char. The char then serves as the primary fuel in the burning process, and the oil vapor and entrained liquid oil flow down along with the exit gas and are pumped to the surface. Suitable collectors, scrubbers, cleaners, and energy recovery units are placed at the surface.

A key factor in the effectiveness of the retorting lies in the method of rubblizing. Ideally one desires nearly uniform, moderate sized particles and uniform gas permeability, so that internal paths for heat transfer and oxygen diffusion to interior of blocks are relatively short and gas flow is relatively uniform across the cross section of the column. The presence of too many fines would result in too high a pressure drop and associated gas pumping cost, and if the oil is held up on the fines, it may also result in oil loss by coking (see below). A significantly large fraction of very large particles would cause loss of oil yield because of the longer heat-up times of the blocks, with the consequent slow release of oil that could burn in a more rapidly moving flame front, unless means can be developed to separate the burning zone from the "retorting" or kerogen-pyrolysis zone.

Objectives

The major objectives of the LLL retorting program are to:

1. Determine phenomena and factors significant to retorting, e.g., kinetics of oil release, kinetics and mechanisms of oil degradation.
2. Attempt to predict optimum operating conditions for commercial in-situ retorts, including methods of control.
3. The ultimate goal is economic recovery of oil under conditions that are environmentally acceptable.

To answer these objectives, we have set up an experimental, calculational and testing program as follows:

1. Pilot retorts (above-ground) well-instrumented and controlled to obtain quality data.
2. A retort computer model based on physical and chemical data, incorporating the most significant phenomena. It is a predictive model, and phenomena observed in our pilot retorts help to guide the modeling.
3. Laboratory experiments to determine oil release, oil degradation kinetics of mineral reactions and char reactions, effects of steam, etc., on powders and single

blocks. Data from these studies are used to further develop the retort model and to clarify pilot retort experimental results.

Results of specific laboratory studies[2-12] and modeling[13,14] efforts are reported elsewhere. Accounts of work on our retorts[15-19] and general experimental results[20,21] have also been reported.

The function of this paper is to present an overview of current understanding of our retorting results to date, to indicate areas that need more understanding and to suggest the direction of our future work.

Pilot Retorts

A description of these retorts and the computers that are used for operation, control, and collection and reduction of data are given elsewhere in more detail.[15-17] For the present purposes, a brief description follows. We have two retorts, one 0.3 m diam. x 1.5 m high (nominally 125 kg capacity) and one 0.9 m diam. x 6 m high (nominally 6000 kg capacity). Both have a series of circumferential heaters spaced 15 cm apart vertically and suitably controlled from our retort computer system. The heaters are programmed to minimize heat losses through the wall to allow us more nearly to simulate in-situ behavior, in which heat losses at the wall boundaries are negligible compared to the axial heat flows in the retorts. Four equally spaced ports at each level provide access for gas sampling and thermocouple probes. The levels are 15 cm apart, and are displaced vertically from the heater positions.

Another important feature of these retorts is a sliding centerline thermocouple which traverses the bed on computer control. This item permits detailed temperature-distance information at frequent times, and supplements data from fixed thermocouples at various levels and radii.

Development

Early work in our pilot retorts established that heater control was necessary to obtain relatively low radial thermal gradients, so that we could make valid data comparisons with our 1-dimensional retort model. We also discovered the effect that heater control had in increasing the rate of retort front advance.[16-17] We developed suitable recovery equipment, since a substantial fraction of the oil product leaves as a mist in the micron-size range.[19] The recovery equipment is described elsewhere,[17-19] and consist of a series of mist separators, condensers and finally a high efficiency filter to capture essentially all the oil.

The many details of our experimental observations in regard to temperatures, gas flows and compositions, heat and mass balances, etc., are being released in a series of reports detailing each retort run (See for example Refs. 18, 19. Other reports will follow.). Therefore, we will limit our discussion here to a summary of our findings to date.

Beds of Uniform Particles

Most of our early work was done in the 125 kg retort, using Anvil Points oil shale of relatively uniform size (+1.3-2.5 cm, approx. 100 l/tonne, or about 24 gal/ton Fischer Assay). A typical plot of temperature vs distance is shown for one of these runs (Fig. 1). More details of operating conditions and results are shown in Table 1.

Retorting results utilizing these relatively uniform sized particles are reasonably well understood. Yields are high, generally close to 95%. Temperature vs distance profiles are smooth and appear close to model predictions, as shown in Fig. 1.[22] Zero time, i.e., at true "beginning" of the run, is hard to define absolutely because some retorting is taking place during ignition and start-up. The model calculation does not take this uncertain transient state into account precisely. Therefore the comparisons shown in the figure between model calculations and measured values were made at those times that gave a close match in the position of the $400^{\circ}C$ point of the retort front. Peak temperatures are also close to model predictions and plots of peak temperature vs bed depth are relatively smooth (Fig. 2).

Other comparisons between experiment and model for a typical run, S-13, are shown in Table 2. Oil yields and retort advance

Figure 1: Temperature vs Bed Depth, Run S-13

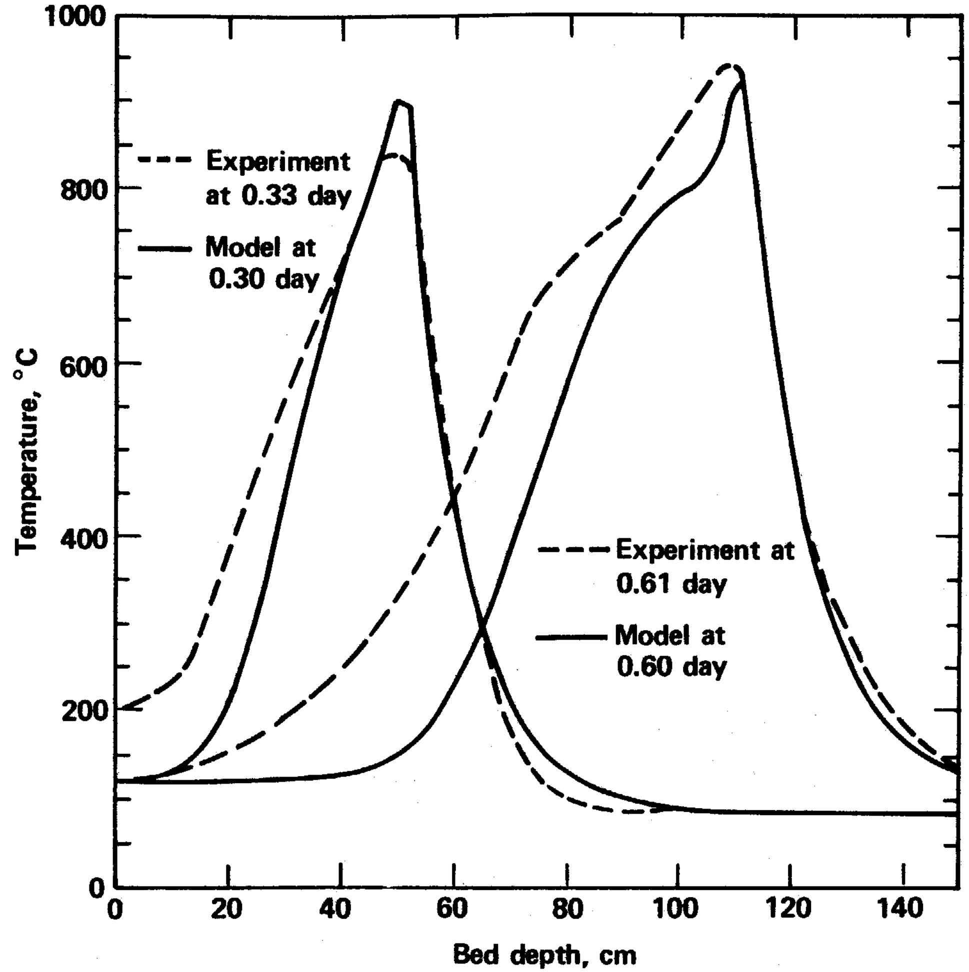


Table 1 Retort run summary, uniform size particles. (-2.5 + 1.3 cm)

Run No.	Gas	Vol, % O_2	Superficial gas veloc. M/min.	Void fraction %	Average retorting rate M/day	Average max. centerline temp °C	Yield, % Fischer assay
S9	N_2	Zero	1.1	47	1.4	494	98.4
S10	Air & recycle	11.8	0.6	47	1.3	868	95.0
S11	Air	21	0.6	47	2.6	1003	92.5
S17	Air + N_2	10.6	0.7	47	1.7	927	92
S13	Air + Steam	10.6	0.7	49	2.2	887	96.3

Figure 2: Peak Temperature vs Bed Depth, Run S-13

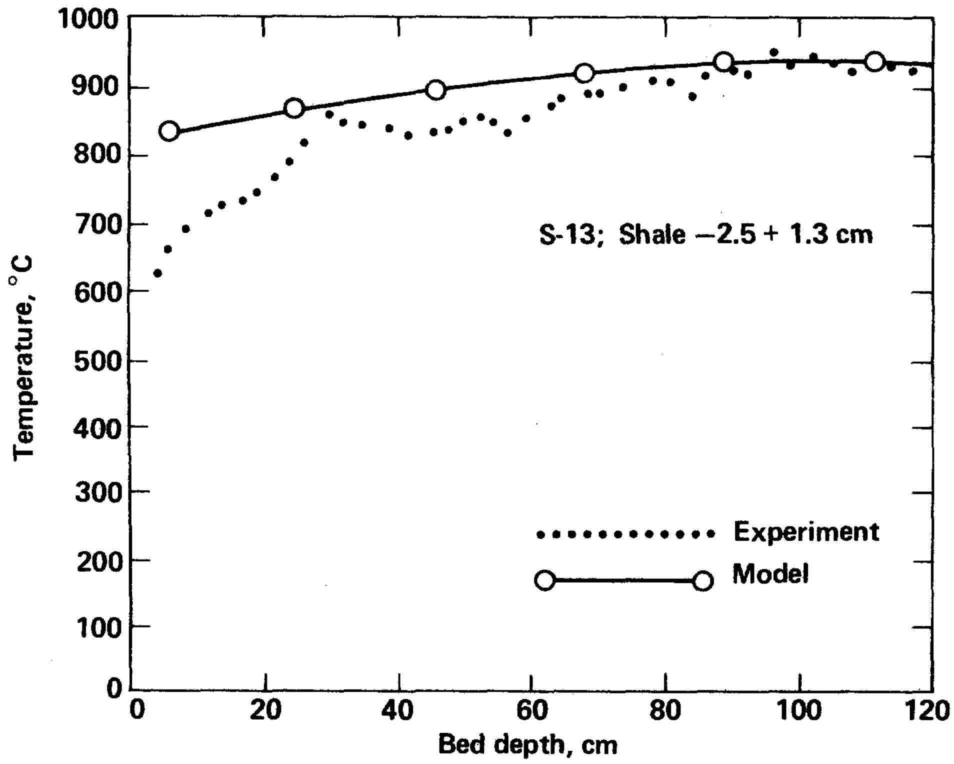


Table 2 Comparison of experimental and calculated results for Run S-13

Input-gas composition	50 vol % air -50 vol % steam	
Input-gas flow rate	0.52 mol/m^2 sec	
Oil shale particle size	-2.5 + 1.3 cm	
	Experimental	Calculated
Retorting rate (m/day)	2.2	2.1**
Oil yield (% Fischer assay)	96	98**
Exit gas composition (vol %) (*)		
H_2	4.7/6.9	3.6
CH_4	1.1	1.0
CH_x	1.0	1.3
CO	1.3/2.4	1.4
CO_2	37.1/35.9	40.9
O_2	0.1	0.0
N_2 + Ar	54.6/52.6	51.8

(*) Ref 17. When two values are given, they represent early stage (excluding startup) and late stage (excluding completion period).

(**) R. Braun, personal communication

rates agree quite well. Compositions of the outlet gas are predicted well, except for H_2 and CO. This may be attributable to the fact that we do not yet have good experimental data on kinetics and stoichiometry of various reactions producing H_2, CO and CO_2, such as combustion of char and oil and the water-gas shift reaction over oil shale: $H_2O + CO = CO_2 + H_2$. Previous work at LLL has shown that the minerals in oil shale show significantly large catalytic effects.[8]

By and large we observe relatively planar flame fronts for these runs, although there is some variability in the tilt of the front (Fig. 7 of Ref. 17).

Effect of Steam

It has been recognized that steam could be a valuable diluent in combustion retorting for several reasons: (1) it has a higher heat capacity and so would drive the retorting front more rapidly; (2) after condensing the steam from the exit gas, one is left with a higher heating value gas; (3) the char-steam ($C + H_2O = CO + H_2$) and water-gas shift ($CO + H_2O = CO_2 + H_2$) reactions yield hydrogen and CO which also raise the heating value of the exit gas. Model calculations show some of these advantages of steam.[13]

Steam as a diluent compared to nitrogen indeed gives higher retorting rates, slightly higher yields, and somewhat lower peak temperatures (See Table 1, Runs S-17 and S-13). Table 3 (below) also shows the effect of substituting steam for nitrogen diluent

Table 3 Effect of steam on exit gas composition

	Run S-13 50 vol % stm 50 vol % air	Run S-17* 50 vol % N_2 50 vol % air
H_2, vol %	4.7/6.9	1.3/1.9
CH_4	1.1	0.6/0.7
C_2	0.4	0.2/0.3
C_3	0.2	0.1/0.2
C_4 +	0.4	0.2/0.3
CO	1.3/2.4	1.5/3.4
CO_2	37.2/35.9	24.1/20.8
O_2	0.1	0.0
N_2 + Ar	54.6/52.6	72.0/72.4
Lower Heating Value kj/mol	48/56	24/39

*J. Raley, private communication

in obtaining exit gas higher in hydrogen, CO, and in heating value, after steam condensation.

Beds of Particles with Non-Uniform Size Distribution

Retorting results from these runs are not well predicted by our model and are characterized by higher peak temperatures, lower yield and evidence of non-uniform gas flow such as irregular and localized hot spots. Results, including particle size ranges used in these runs are given in Table 4. Particle size distributions are given in the Appendix, Figs. 6-9.[23] Particle size distributions for Runs S-12 and S-18 are similar to those for S-14 (Table 4). Run L-1 was done in the large (6000 kg) retort. All others (prefixed "S") were done in the small retort (125 kg). Results in the large retort having much larger particles (up to 30 cm) showed greater departure from the uniform and "predictable" behavior of uniform size particle beds, than those from small retort runs having smaller particles (up to 7.5 cm).

Summarizing results for beds of non-uniform particles:

1. Gas flow non-uniformities were obvious. At a particular cross section we observed wide variations in temperature and oxygen content. This was especially obvious in Run L-1, in which two probes were placed at the same level of the bed, one 2 cm below a large (30 cm) block, the other 40 cm away in 0 to 7.6 cm rubble. The latter reached peak temperature 30 hours after the former

Table 4 Retort run summary, non-uniform size particles.

Run No.	Gas	Vol % O_2	Superficial gas veloc. M/min	Void fraction %	Particle size range, cm	Average retorting rate, M/day	Average max. C_L temp, °C	Yield, % Fischer assay
Large retort run								
L-1	Air + N_2	8.7	1.1	25	-7.6 + 0 + 30 cm blocks	1.7	995 (900-1200)	72
Small retort runs								
S-12	Air + N_2	8.9	1.1	38	-7.6 + 0	2.1	942	92.6
S-14	Air + Steam	10.6	0.7	34	-7.6 + 0	1.6	1010	88
S-15	Air + Steam	10.6	0.7	37	-2.5 + 0	1.5	1025	86
S-18	Air + Steam	10.6	0.7	33	-7.6 + 0	1.3	1005	91
S-16	Air + Steam	10.6	0.7	43	-0.34 + 0.085	1.8	980	99

(Fig. 3).[17] Similarly oxygen appeared at the latter probe about 35 hours after reaching the probe near the block, confirming preferential gas flow near the large block. This flow also accelerated the pyrolysis reactions in the large block. Similar observations of temperature differences at particular levels were also observed.[17]

2. Yields are moderately lower on average than for the uniform particle cases, viz., 86-92% vs 92-96%, except for Run L-1 which had a substantially lower yield (72%). The major difference in Run L-1 was the presence of a major fraction (39%) of large blocks (ca. 30 cm).
3. Unlike the smooth temperature vs distance plots observed for uniform particles, these plots showed irregularities and at times multiple peaks for runs of non-uniform particles. The most severe case again was L-1 in which multiple peaks were most pronounced (Fig. 4).[16]
4. Peak temperatures were considerably higher (100-150°C) for these runs than for comparable runs with uniform size shale (-2.5+1.3 cm). Similarly, they were higher than those predicted by the retort model. Furthermore, peak temperatures showed considerable fluctuation with distance. Figure 5 shows the results for S-15. Run S-14 showed similar effects. Contrast Fig. 5 with Fig. 2 for Run S-13 having uniform particles.

Figure 3: Temperature and Oxygen vs Time, Run L-1

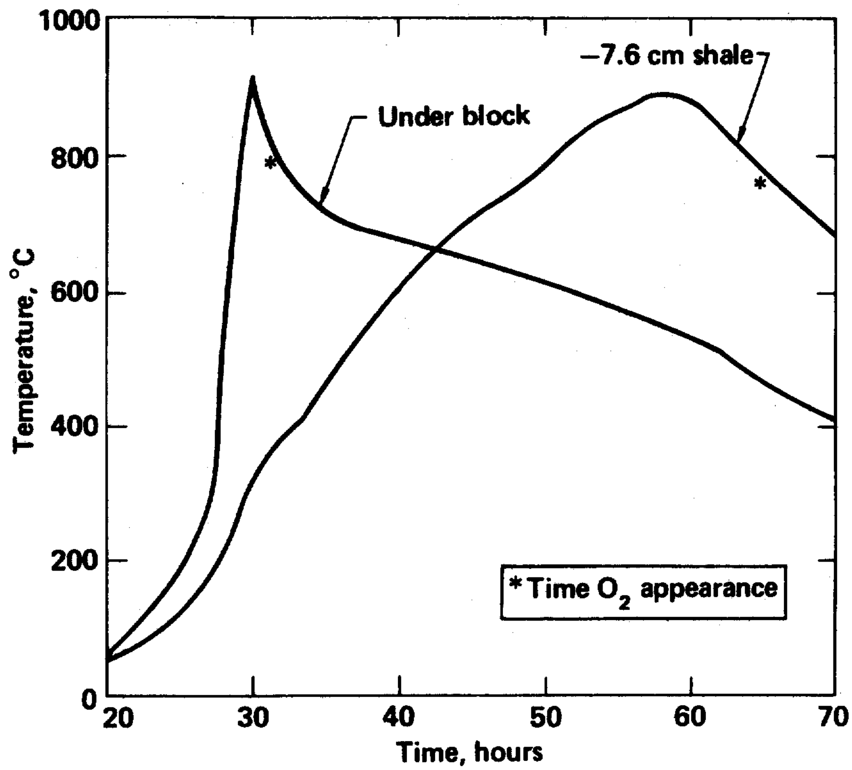


Figure 4: Temperature Profiles at Various Times for Large Retort Run L-1

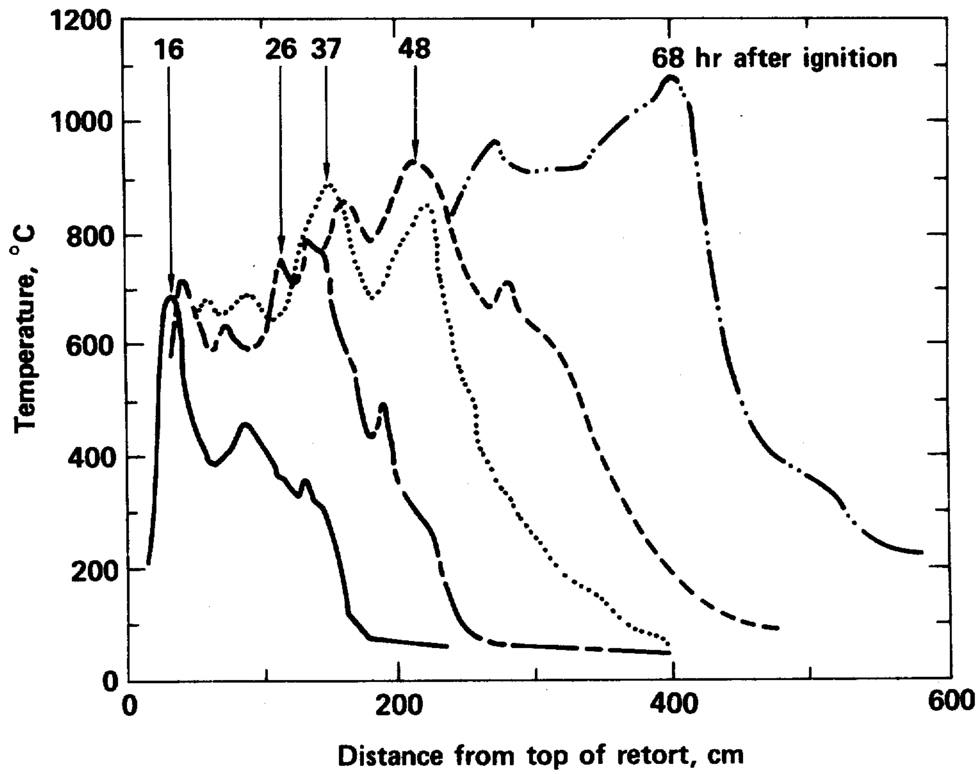
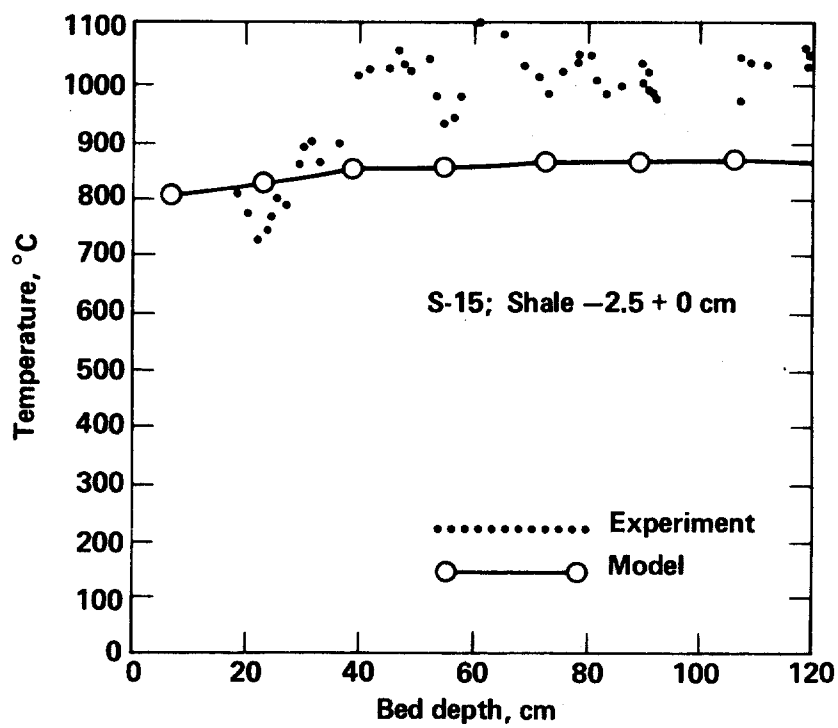


Figure 5: Peak Temperature vs Bed Depth, Run S-15



5. We attempted to construct beds approaching the low void fractions expected in-situ. Therefore particle packing was done in such a way as to produce inadvertently some layering of fines. To determine the effect of more random packing Run S-18 was run to duplicate S-15, in which layering was suspected. Results were similar for both, except that a slightly higher oil yield and a lower retort rate was observed in S-18 (Table 4). It is not clear that these differences are significant.

Several hypotheses are advanced for the behavior observed for particles with non-uniform size distribution. One is that gas flow non-uniformity is a function of the variable local permeability when using multiple particle sizes. A second hypothesis is that more oil is held up in beds containing fines, increasing pressure drop and exacerbating differences in gaseous permeability. Oil holdup provides still another mechanism for loss of yield, viz., it permits vaporization of the light oil ends as a hot gas front approaches. The heavier oil remaining is viscous and so may readily char as still hotter gas approaches. (The char is eventually burned, and so evidence for its presence is lost.)

Run S-15 (-2.5+0.0001 cm particles) was carried out using a much larger proportion of fine material and so had a much smaller D_p = 0.676 mm (surface-area equivalent particle size) than S-14 (D_p = 1.963 mm). The oil holdup, determined by the time at which oil first appeared below the column, was appreciably greater for S-15 than for S-14, viz., 60% vs. <50%[17] (estimated as 30-35%). Yet the oil yields and temperature behavior were not significantly different (Table 4).

Run S-16 was made in an attempt to determine whether fine particles per se caused the behavior described above in the absence of a broad distribution of particles. A relatively narrow cut of particles, viz., -0.34+0.085 cm was used having a D_p (1.763 mm) close to that of S-14. Run S-16 had a high yield (99%), and showed no "structure" in its temperature-distance plots at various times or in its peak temperature vs distance plots. This result provides additional evidence that fines, at least down to the size used in this run, do not have a major impact on oil loss. One minor reservation is that the void fraction was larger in Run S-16 than in S-14 (43% vs 34%). We would expect the effect of oil holdup to be larger as void fraction is reduced. Another unexplained issue is that peak temperatures observed in S-16 were about 100°C above those calculated by our model.

Significance of Non-Uniform Behavior

The key question is: what are the factors and conditions reducing oil yield? In our small retort, we have obtained yields not much lower than those obtained for uniform (1.3 to 2.5 cm) particles, at least using beds containing particles up to 7.5 cm. As a consequence we have been looking at other types of behavior that we assume are associated with potential loss of yield. They are: (1) evidence of non-uniform gas flow, (2) irregular temperature vs distance plots and (3) fluctuating peak temperatures vs distance down the retort. Also (4) these temperatures are significantly higher than predicted by modeling. The evidence of Run L-1 indicates that these four observations are associated with yield loss, perhaps because of oil burning.

The effects of gas flow non-uniformity have been described above for L-1. It is apparent that enhanced gas flow due to higher permeability in the vicinity of a block may cause early and rapid heating at the surface of a block and burning of kerogen and oil as oxygen appears. Clearly this could be an important mechanism for yield loss.

The issues related to liquid flow and holdup in rubble beds were discussed above. In in-situ retorts it is expected that fines will be a much smaller fraction of the shale than we have used in Runs S-14, -15, and -18. However, in the runs cited here, the void fraction was 33-37%. We anticipate void fractions of 20-25% <u>in-situ</u> and even less if appreciable deformation of hot shale columns occur.[24-26] In those cases the effect of oil holdup on gas flow and yield loss would be magnified, and may play a significant role in yield loss.

To determine how to improve yields and control temperatures observed in beds of particles having wide size distribution, more runs will be required using larger particles at the upper end of the distribution. Clearly the substantial reduction in yield of L-1 is attributable to the presence of 30 cm particles. We could then determine the effect of operating variables such as air flow rate and steam/air ratio on the yield.

Other work is proceeding to clarify the effect of bed structure on gas flow patterns, including the use of gaseous tracers. Results are not yet available.

Conclusions

1. Retorting of a bed of small (1-2 cm) uniform oil shale particles gives high oil yields (92-98%) and reasonably well-understood and predictable behavior in temperatures, retorting front advance rates, and gas compositions.

2. The use of steam as a diluent in retorting gives modest improvement in oil yield and retorting front advance rate, and heating value of the outlet gas. Hydrogen in the outlet gas is considerably enhanced by the use of steam, from the steam-char and water gas shift reactions.

3. Retorting of beds of non-uniform particles shows somewhat lower oil yields, irregular temperature vs distance profiles and higher temperatures than predicted by a one-dimensional retort model. It is believed that the above behavior is due primarily to non-uniform gas flow perpendicular to the bed cross-section.

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Acknowledgement

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APPENDIX

Figure 6: Particle Size Plot, Run S-14

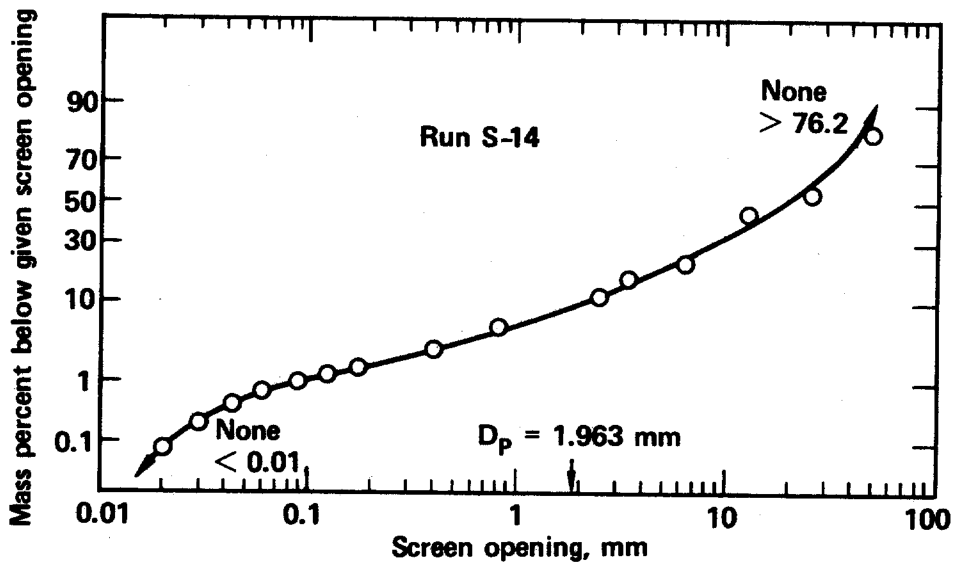

Figure 7: Particle Size Plot, Run S-15

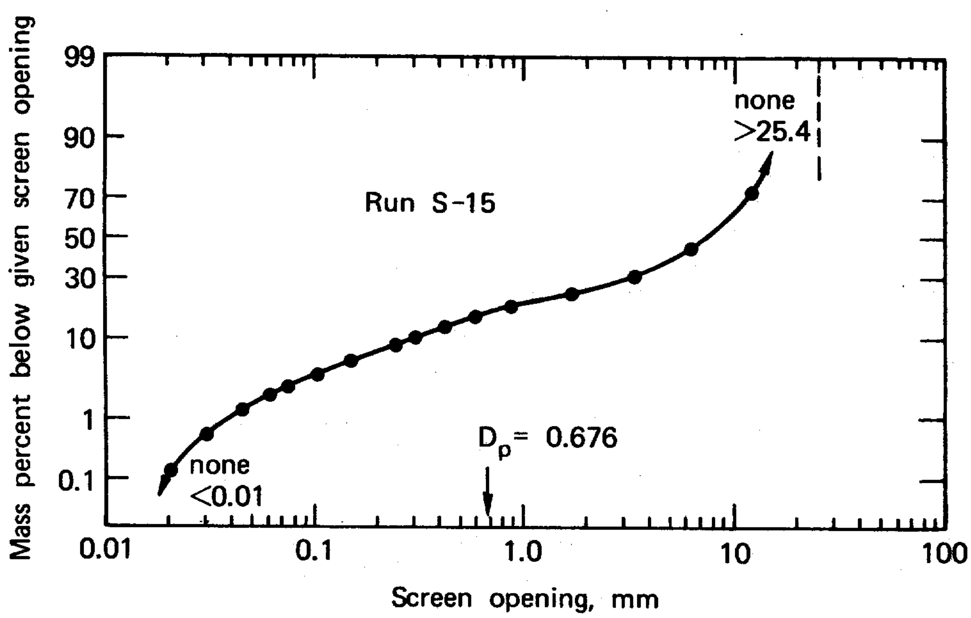

Figure 8: Particle Size Plot, Run S-16

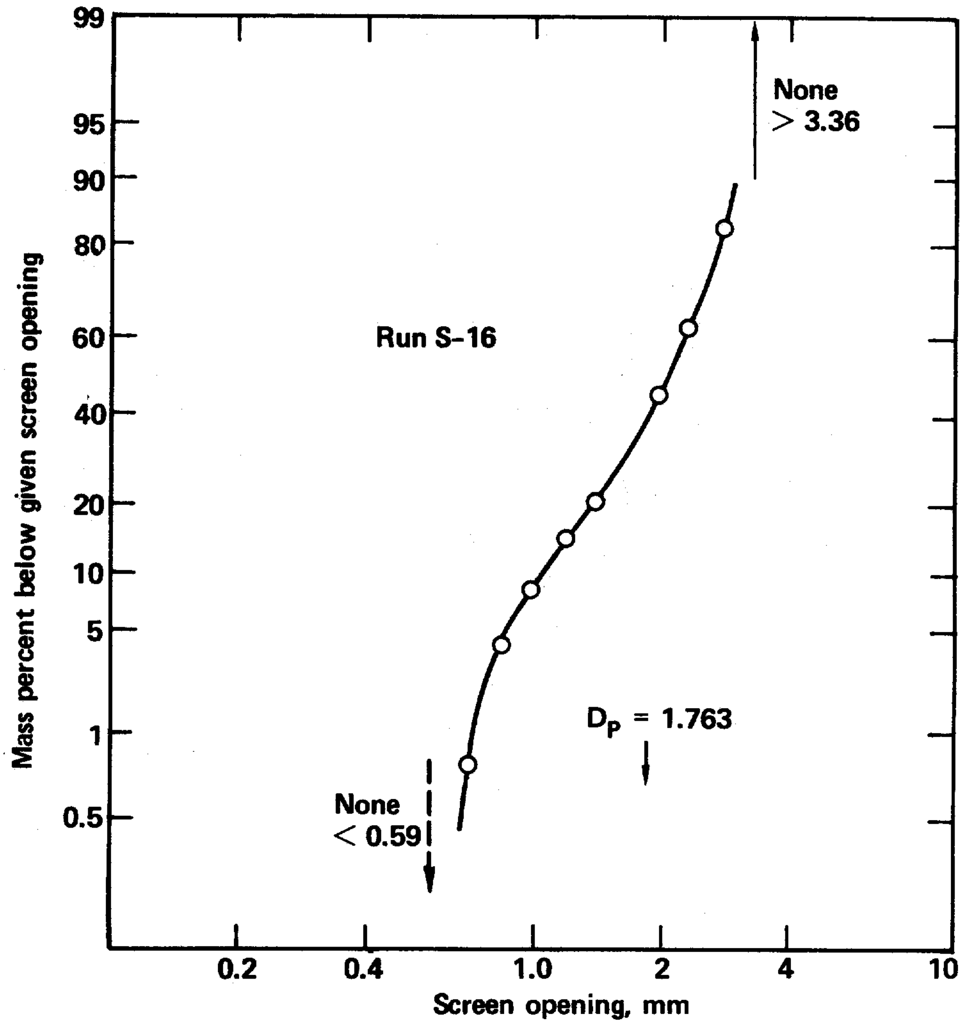

Figure 9: Particle Size Plot, Run L-1